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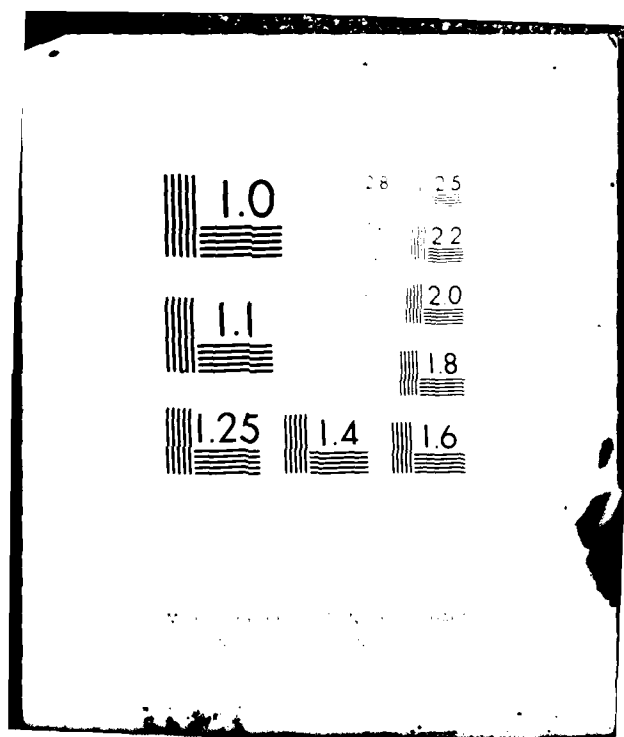
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Technical Report #27

Rotational and Spin-State Distributions:
NO Thermally Desorbed from Ru(001)

Richard R. Cavanagh and David S. King

Molecular Spectroscopy Division
National Bureau of Standards
Washington, DC 20234

March 3, 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Rotational state distributions have been measured for the first time in molecules thermally desorbed from a metal single crystal. Laser excited fluorescence has been used to monitor, under ultrahigh vacuum conditions, the desorption of NO from Ru(001). The population distribution for those states with less than 400 cm^{-1} of rotational energy (including spin) can be represented by a single Boltzmann factor, $T_{\text{rot}} = 235 \pm 35 \text{ K}$, significantly lower than the surface temperature at the desorption maximum, $T_s = 455 \pm 20 \text{ K}$.		

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by

Richard R. Cavanagh and David S. King
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Washington, D.C. 20234

Abstract

Rotational state distributions have been measured for the first time in molecules thermally desorbed from a metal single crystal. Laser excited fluorescence has been used to monitor, under ultra-high vacuum conditions, the desorption of NO from Ru(001). The population distribution for those states with less than 400 cm^{-1} of rotational energy (including spin) can be represented by a single Boltzmann factor, $T_{\text{rot}} = 235 \pm 35\text{ K}$, significantly lower than the surface temperature at the desorption maximum, $T_S = 455 \pm 20\text{ K}$.

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One of the severe obstacles in theoretically modeling the dynamics of reactive processes occurring at a gas-surface interface is the absence, until very recently, of experimental data on the details of the partitioning of energy within the incoming or exiting gas phase species¹. Such state to state studies of bimolecular gas phase processes have resulted in a detailed understanding of potential energy hypersurfaces and of molecular dynamics². It is now becoming practical to apply sensitive internal state specific diagnostics (e.g., laser excited fluorescence) to the study of chemical reactions and molecular energy transfer on well-characterized metal single crystal surfaces.

To date, two types of gas-surface experiments have been examined: heterogeneous reaction and inelastic molecular scattering. Under the classification of heterogeneous reaction, most systems studied exhibit a significant barrier to the reverse reaction (adsorption). This barrier provides the exiting molecular species with excess energy which can appear as vibrational³, translational^{4,5}, or rotational⁶ excitation. In the inelastic scattering experiments a high degree of energy accommodation (i.e., nearly full equilibration with the surface) has been associated with trapping/desorption, while lower degrees of accommodation have been thought to indicate direct impact-type interactions⁷. Laser excited fluorescence (LEF) measurements of the rotational distribution of NO molecules scattered from NO or graphite covered Pt(111)⁸

and clean, single crystal Ag(111)⁹⁻¹¹ have shown that the rotational state populations can be described by Boltzmann-like distributions. The degree of accommodation is strongly dependent on the nature of the surface.

In this paper we report the first measurements of a nascent internal energy distribution obtained from thermal desorption experiments from a single crystal metal surface under ultra-high vacuum (UHV) conditions. The experiment consisted of measuring the density, via laser excited fluorescence (LEF), of the resulting gas phase NO species in various rotational levels (J'') of the ground $\tilde{X}^2\Pi_{1/2,3/2}$ electronic state. Since molecular NO evolution only occurs during the 5-10 second period that the temperature increases from 435 to 475 K, only one level can be probed during each temperature programmed desorption (TPD). This system was chosen for study for two significant reasons. First, Ru(001) is highly reactive to NO, and therefore this system will provide a useful complement to the nonreactive NO/Ag(111) system⁹⁻¹¹. Second, the surface properties of this system have been studied extensively. The vibrational modes of the adsorbed NO¹², the thermal desorption spectrum^{13,14}, and the coverage dependence of binding site occupation¹³ have been well established.

The sample chamber used in this work is a stainless steel UHV ($P \leq 4 \times 10^{-10}$ torr)¹⁵ apparatus equipped with an ion pump, titanium sublimators, effusive molecular beam doser, and quadrupole mass spectrometer. The Ru(001) crystal was mounted on a rotatable manipulator and

could be cooled to 180 K with nitrogen or heated to 1670 K by conduction from resistively heated tantalum support leads. The Ru crystal was cleaned by repeated heating in O_2 in front of the doser at 1390 K followed by flash annealing to 1660 K to remove residual oxides. This cleaning procedure has been shown to reproducibly yield¹² clean surfaces. The quadrupole mass spectrometer was used to establish the NO exposure at the doser required to saturate the 0.5 cm^2 crystal at 273 K. All TPD reported herein were obtained following saturation coverage of the freshly cleaned and cooled Ru crystal and for a heating rate of 12 K sec^{-1} .

The thermally desorbing NO was probed by a laser beam of $40 \text{ }\mu\text{J}$, 0.1 cm^{-1} spectral bandwidth (FWHM), and 10 ns pulse duration, tunable about the origin of the $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi_{1/2,3/2}$ transition at $44,140.78 \text{ cm}^{-1}$ (in NO, the two spin components of the ground state are split by 123.2 cm^{-1} due to spin-orbit coupling)¹⁶. After traversing the UHV system, the probe laser passed thru a NO gas phase reference cell into an absolute energy meter. The ultraviolet (u.v.) beam was well collimated over the 1 m path length with a beam area of 0.06 cm^2 . In the UHV system the laser beam passed parallel to the surface plane with its center 0.5 cm from the crystal surface. The LEF signals resulting in the UHV system and reference cell were detected in comparable fashion, using 1P28-B type photomultiplier tubes (PMT). The reference cell gas was a 46 ppm mixture of NO in dry nitrogen¹⁷, flowing thru the cell at a total pressure of 50 mtorr. Typically the reference cell LEF intensity

was attenuated 10^3 fold by u.v. neutral density filters to make the reference signal comparable to the thermal desorption LEF. The output of the two PMTs were fed into a matched pair of gated integrators, digitized, ratioed and accumulated in a multi-channel averager.

Figure 1 (top trace) shows typical data obtained for a single TPD while probing a single rotational state. The maximum in the laser detected thermal desorption spectrum occurs at 455 K and corresponds to a peak $\text{NO}(J'' = 6\ 1/2)$ density of $2 \times 10^6\ \text{cm}^{-3}$. For comparison, a thermal desorption spectrum at $m/e = 30$ monitored by the mass spectrometer is presented. Desorption experiments conducted with the crystal rotated to be 3 cm below the laser beam indicated that contributions from NO which had undergone wall collisions were insignificant in the gettered system (base line LEF trace). Each TPD resulted in a single measurement of the NO density in one particular spin-rotation state. As the Ru crystal was being cycled through the annealing/dosing procedure¹² the laser wavelength was tuned to probe a new, randomly selected J'' . The LEF signal observed while exciting a specific $J' + J''$ transition is dependent on: the population density $^{\text{TPD}} N_{J''}(t)$ at the time of the laser probe, a line strength (e.g., Hönl-London factor) for that transition, the laser energy and overlap of the laser frequency and bandwidth to the Doppler broadened ro-vibronic line profile, and detection efficiency factor. To minimize potential errors arising from random fluctuations in laser energy, frequency, and bandwidth, the reference cell LEF was always recorded simultaneously during TPD. The recovered, ratioed signal

$I_{J''}(t)$, observed at time t during the TPD is simply:

$$I_{J''}(t) = \frac{TPD_{N_{J''}}(t)}{ref_{N_{J''}}} \times C_{rel}^{-1} \quad (1)$$

where C_{rel} is the relative detection efficiency for the two optical systems. Since the reference cell is at thermal equilibrium, $ref_{N_{J''}}$ is proportional to $(2J'' + 1) \exp(-E_{J''}/k^{ref}T)$, where $E_{J''}$ is the rotational level energy and $^{ref}T = 293$ K. In figure 2 we have plotted the relative probability, $P(J'')$, of a thermally desorbed NO molecule having total rotational energy (including spin) of $E_{J''}$. The quantity $P(J'')$ is defined by:

$$P(J'') \equiv \frac{TPD_{N_{J''}}(max)}{(2J'' + 1)} = I_{J''}(max) \exp(-E_{J''}/k^{ref}T) = C_{rel}^{-1} \exp(-E_{J''}/k^{TPD}T) \quad (2)$$

The rotational state populations in the lower lying $^2\Pi_{1/2}$ spin component were obtained monitoring $Q_{11}(J'')$ and $R_{11}(J'')$ branch transitions; in the $^2\Pi_{3/2}$ component, the $Q_{22}(J'')$ branch was measured. Each data point in figure 2 represents the average of some 10-15 individual TPD measurements, each with an individual S/N ratio of 10, and incorporates data taken during runs on several days. To the extent that the rotational state population distribution of the thermally desorbing NO can be characterized by a Boltzmann distribution one would expect a linear plot of $\ln P(J'')$ against $E_{J''}$, defining a rotational temperature T_{rot} . The data, plotted in this fashion in figure 2, gives a linear regression

correlation coefficient of -0.98 for all points $E_{\text{rot}} \leq 400 \text{ cm}^{-1}$ indicating the thermally desorbed NO to be accurately described by a Boltzmann rotational temperature. A least squares analysis gives $T_{\text{rot}} = 235 \pm 35\text{K}$ (95% confidence level).

The important result of this work is that the distribution of total rotational energy (including electronic spin) of those NO species desorbing from singly coordinated sites on Ru(001) at $455 \pm 20\text{K}$ is well represented by a single Boltzmann temperature $T_{\text{rot}} = 235 \pm 35\text{K}$ significantly lower than the surface temperature.

Although the construct of an adsorbed yet highly mobile, freely rotating activated complex has proven useful in modeling certain surface reactions (including desorption¹⁸), if the desorbing NO were to pass through such a precursor state, a rotational temperature in the nascent gas phase NO equal to the surface temperature should result. This is not observed experimentally. Our measurements indicate an integrated NO flux of only 2-6% of a monolayer during TPD from an initially clean crystal. The dissociated species could provide a barrier to free migration of the remaining atop-bound molecular NO. We believe, therefore, that the gas phase NO is derived directly from a well-characterized chemisorption state. The small degree of rotational energy in the NO fragment apparently results from dynamical effects occurring along the exit channel of the molecule-surface potential energy hypersurface. Most simply, this result is consistent with a weakly non-central repulsive force and a negligible barrier (i.e., $1\text{-}2 \text{ Kcal mole}^{-1}$) to the reverse adsorption process. In addition, we find the observed equilibrium

between electronic spin (S) and the resultant of orbital and nuclear rotational angular momenta (K) striking. This equilibrium indicates that the nuclear rotational angular momentum and electronic spin both develop in the same region of the potential energy surface.

These experiments, as compared to static surface spectroscopies, provide the first measurements which directly probe the chemisorption-bond making/breaking region of the adsorbate/substrate potential energy hypersurface⁸⁻¹¹. Careful analysis of the internal state distributions of molecules interacting with well-characterized surfaces involving either negligible exit channel barriers (as in the NO/Ru(001) system) or more strongly repulsive interaction potentials will stimulate theoretical efforts aimed at understanding molecule-surface dynamics.

It is our pleasure to thank John T. Yates, Jr. for suggesting the temperature programmed desorption experiment and John C. Stephenson for his critical comments and many useful discussions. This work was supported in part by the Office of Naval Research.

Figure Captions

Fig. 1: Laser excited fluorescence and mass spectrometer detected thermal desorption spectra. Each trace is the result of a single temperature programmed desorption. The base line LEF trace is the observed signal when the crystal is rotated to be 3 cm below the laser beam.

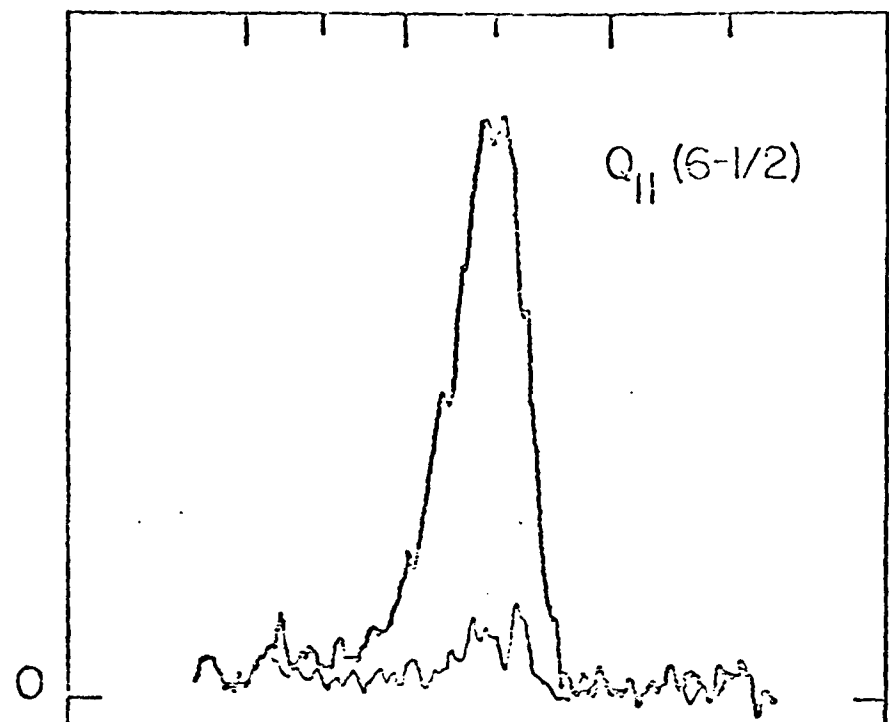
Fig. 2: Rotational and spin state population distribution for NO thermal desorption from Ru(001) at 455 ± 20 K. A single Boltzmann temperature, $T_{\text{rot}} = 235 \pm 35$ K, describes the total angular momentum distribution. The various symbols represent population densities, as defined by eqn. (2) in the text, for excitation on the $R_{11}(J'')$ (circle), $Q_{11}(J'')$ (triangle), and $Q_{22}(J'')$ (square) branch transitions.

References

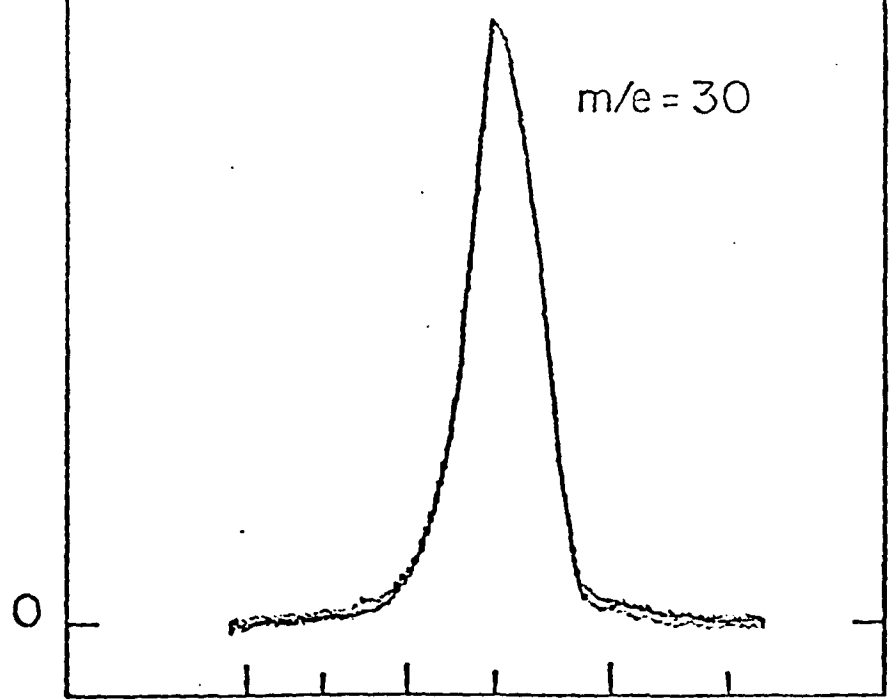
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LASER EXCITED
FLUORESCENCE



MASS SPECTROMETER ION
SIGNAL



300 400 500
CRYSTAL TEMPERATURE
 T_s (K)

RELATIVE POPULATIONS

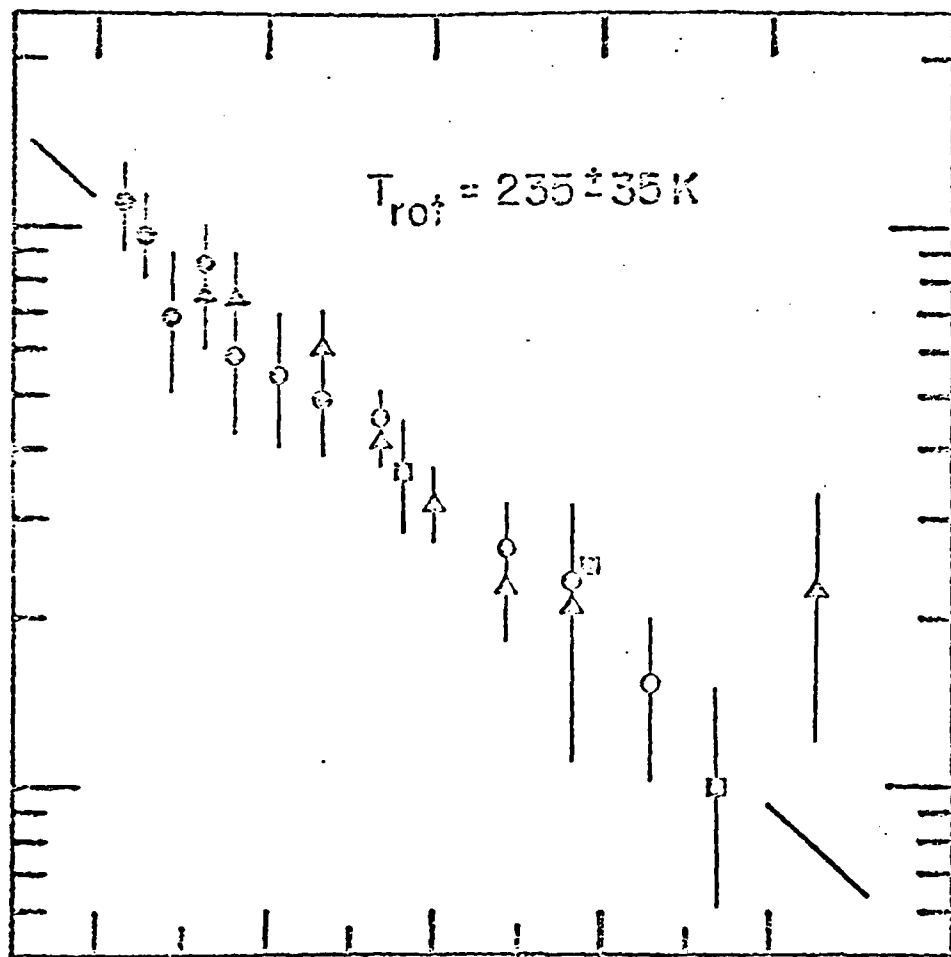
$P(J'')$

$T_{\text{rot}} = 235 \pm 35 \text{ K}$

0 100 200 300 400

ROTATIONAL ENERGY

$E_{J''} \text{ (cm}^{-1}\text{)}$



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